

RECOVERY OF SALEABLE SALTS FROM OCCURRING NATURAL BRINES REPRESENTING THE QUINARY AQUEOUS SYSTEM Na-K-Mg-Ca-Cl

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Abstract

Potassium chloride (KCl) accounts for most of the potassium (K) used in world agriculture and represents 96% of the world potash capacity. The other 4% includes potassium sulfate (K_2SO_4), potassium nitrate (KNO_3) and potassium-magnesium based salts. In this sense, the prediction of the solubility of electrolytes in aqueous solutions is important to provide data for processes that extract potassium salts from multicomponent brines. In this work, Pitzer's and Harvie's models were used to calculate the amount and composition of crystallized salts after water evaporation. The process involved four crystallization steps starting from multicomponent brines represented by the quinary Na-K-Ca-Mg-Cl aqueous system at 20°C. The temperature of 20°C was chosen because it is the average process brine temperature in many dry salt lakes. The Pitzer's and Harvie's models allowed performing a material balance in solar ponds producing saleable salts like sodium, potassium, magnesium and calcium chlorides.

Keywords: Crystallization; Potassium; Quinary Na-K-Ca-Mg-Cl Aqueous System.

RECUPERAÇÃO DE SAIS COMERCIAIS A PARTIR DE UMA SALMOURA NATURAL REPRESENTATIVA DO SISTEMA QUINÁRIO Na-K-Mg-Ca-Cl

Resumo

O cloreto de potássio (KCl) é uma das principais fontes de potássio (K) usada na agricultura e corresponde a 96% do consumo mundial desse nutriente. Os outros 4% incluem o sulfato de potássio (K_2SO_4), nitrato de potássio (KNO_3) e os sais duplos de potássio e magnésio. A previsão da solubilidade dos eletrólitos em soluções aquosas é importante na estimativa dos parâmetros de processos da rota de processo a ser usada na extração seletiva dos sais de potássio presentes em salmouras multicomponente. Nesse sentido, os modelos de Pitzer e Harvie foram usados nas estimativas das quantidades e das composições dos sais cristalizados após evaporação da água. A rota de processo envolve quatro etapas de cristalização de uma salmoura representativa do sistema aquoso quinário Na-K-Mg-Ca-Cl na temperatura de 20°C. A temperatura de 20°C foi escolhida por ser a temperatura média das salmouras verificadas nos salares Andinos. Os resultados obtidos com os modelos de Pitzer e Harvie permitiram a elaboração do balanço de massa e energia das piscinas de evaporação e obtenção dos sais comerciais: cloretos de sódio, potássio, magnésio e cálcio.

Palavras-chave: Cristalização; Potássio; Sistema Aquoso Quinário Na-K-Ca-Mg-Cl.

I INTRODUCTION

The knowledge of solubility of electrolytes in aqueous solutions is essential for the development of many processes such as brines and seawater desalination, salting-out

crystallization and liquid-liquid extraction in chemical, mineral and hydrometallurgical industries [1]. For example, high evaporation rates and minimal rainfall in northern regions

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of Argentina and Chile allow solar evaporation ponds to produce commercial salts from natural brines, like potassium chloride, potassium sulfate and lithium salts [2].

The processing of brines from Qarhan Salt Lake (China) containing K^+ , Na^+ , Mg^{+2} and Cl^- follows the crystallization sequence: $NaCl \rightarrow NaCl + KCl \rightarrow NaCl + KCl \cdot MgCl_2 \cdot 6H_2O \rightarrow NaCl + KCl \cdot MgCl_2 + MgCl_2 \cdot 6H_2O$. In this process, during carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) formation step, NaCl is always associated with carnallite as mixed crystals. Therefore 12-25% w/w NaCl has to be separated first in order to produce pure KCl by carnallite decomposition [3]. Similarly, all resulting multicomponent brines have to be processed to deliver the individual salts with purities compatible with market-grade products.

Thermodynamic models are a usual tool to design and evaluate the facilities that produce salts with market-grade purities. For example, the Pitzer and Harvie's model agrees well with literature data on both: the binary systems ($NaCl-H_2O$, $KCl-H_2O$ and $MgCl_2-H_2O$) and on the ternary systems ($NaCl-KCl-H_2O$) at 20°C as already published [4]. The process is based on the separation of inorganic salts from a multicomponent system using fractional crystallization [5]. To this end, Pitzer's ion-interaction model [6] and its extended Harvie and Weare's model [7,8] are suitable tools, because they are reliable in predicting the mineral solubility of multicomponent salt systems in natural waters with high ionic strength (0 to 6 molal), over a wide range of temperatures (0 to 300°C) [8-10].

A complete study for the system Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O was carried out at 25°C by Harvie et al. [7]. The authors used the salts solubilities in the ternary ion system to obtain the mixture parameters and also to determine the chemical potentials of some of the solid phases. A similar procedure was used to predict the solubilities of the Na-K-Mg-Cl-SO₄-OH-H₂O system at several temperatures [9]. The equations for the calculation of the solubilities of halite, sylvite and carnallite, individually or combined, have been set up by Marcus and Soffer [11] for the quinary system NaCl-KCl-MgCl₂-CaCl₂-H₂O at 25°C.

Thus, the objective of this study is to understand the equilibrium of the quinary aqueous system Na-K-Mg-Ca-Cl, using synthetic pulps with different amounts of NaCl, KCl, MgCl₂·6H₂O and CaCl₂·2H₂O analytical grade salts. To this end, solubility data measured at 20°C for liquors and solids in equilibrium, representing the aqueous Na-K-Mg-Ca-Cl system, were compared with the solubilities calculated based on Pitzer's and Harvie's ion-interaction models. The idea was to verify the capability to predict the behavior of the system after the removal of different amounts of water by evaporation. The motivation behind this study is to obtain data to help in evaluating the technical and economic feasibility of operations in natural occurring brines, representing the aqueous Na-K-Mg-Ca-Cl system. The purpose would be to obtain saleable salts, like magnesium and calcium chlorides, as well as sodium and potassium chlorides, at grades matching market specifications.

2 METHODOLOGY

Phase equilibrium at 20°C in the quinary system was studied using the isothermal dissolution method [12]. Batch crystallization experiments with synthetic pulps were conducted using a thermostatic shaker from Innova 44 model New Brunswick, with temperature controlled to 0.02K. Analytical grade salts from Merck: sodium chloride (NaCl, 99.5 wt%), potassium chloride (KCl, 99.5 wt%), magnesium chloride (MgCl₂·6H₂O, 99.5% wt%) and calcium chloride (CaCl₂·2H₂O, 99.5 wt%) and double-deionized water were used to prepare the various slurries. Stirring was provided by a mechanical stirrer at 200 RPM, using a 45° pitched blade impeller. Table 1 shows the amount of salts used to prepare the exploratory five synthetic pulps. All pulps were saturated with NaCl. The difference of the three first pulps was the amount of water to evaluate the effect of water in the crystallization by evaporation. The fourth pulp had a reduced amount of NaCl in order to evaluate the behaviour of KCl, MgCl₂ and CaCl₂ and, in the fifth, the amounts of NaCl and KCl were reduced to analyse the behaviour of MgCl₂ and CaCl₂.

The pulps were distributed in five recipients and stirred for 48 hours at 200 RPM in order to achieve equilibrium. The pulps in equilibrium at 20°C were vacuum filtered using 0.22 μm membranes. The temperature of 20°C was chosen because it is the average process brine temperature in most salt lake operations [2].

The liquid phases were diluted with double-deionized water to determine the sodium, potassium, magnesium and calcium contents with a GBCPlus Atomic Absorption Spectrometer. The chloride concentrations in the liquid phases were determined by titration with a standard solution of AgNO₃ in the presence of drops of 0.1% (w/v) K₂CrO₄ as an indicator.

Solids samples for X-ray diffraction were ground below 200 # TYLER MESH and analyzed on a PANalytical Model X'PERT PRO MPD (PW 3419) with a PW3050/60 (θ/θ) goniometer, X-ray ceramics tubes, anode of Cu ($K\alpha_1 = 1,540598 \text{ \AA}$) and PW3373/00 model (2000 W-60kV). Diffraction patterns were acquired from 5° to 75°, 2θ at 0.02 steps. The identification of all minerals was done with X'Pert High Score version 2.1b software from PANalytical.

Table 1. Amounts of salts and water used to prepare the five synthetic pulps

Test Number	NaCl (g)	KCl (g)	MgCl ₂ ·6H ₂ O (g)	CaCl ₂ ·2H ₂ O (g)	H ₂ O (g)
1	57.47	4.05	14.16	18.23	188.02
2	57.47	4.05	14.16	18.23	88.02
3	57.47	4.05	14.16	18.23	68.02
4	0.70	4.05	14.16	18.23	28.02
5	0.70	0.05	14.16	18.23	8.01

RESULTS AND DISCUSSION

The results are shown in two separate sections. In the first, the solubilities of interest are calculated using the thermodynamic models and the experimental data are compared to the solubilities calculated by the models. In the second section, a material balance for a solar evaporation pond is developed to estimate the production of market-grade salts.

3.1 Solubility Predicted by Pitzer's and Harvie's Models

The theory used to calculate the salts solubilities was described by Silva et al. (2016) according to reference [4]. Experimentally determined equilibrium compositions of liquid and solids phases from five synthetic pulps are shown in Table 2 and Table 3. The Pitzer's and Harvie's models results are presented in Table 4.

From Table 2 and Table 4, it is seen that the liquid phases obtained from tests 1, 2 and 3 are all saturated with NaCl, while the low NaCl contents, in the solid salts from

tests 4 and 5, could be due to their respective impregnated liquid phases. The high amount of solids in equilibrium with the respective brine was founded in test 4, 11% w/w of brine and 89% w/w of solids. The equilibrium liquid phase from test 5 is saturated with respect to several salts, as indicated in Table 3 and Table 4. It is noticed the presence of the most soluble salts, carnallite and calcium chloride included, in the solid phases of test 4 and test 5, respectively. Table 4 presents the values of activities of water (a_w), calculated by equation 6 from reference [11], for the five liquid phases in equilibrium with the solids in each test. It is possible to check a reduction of water activity with the increase of total soluble solids.

Figure 1 shows a comparison between the compositions of equilibrium brines at 20°C calculated by Pitzer's and Harvie's models and obtained by the tests with synthetic pulps.

The simulated and experimental results of the synthetic pulps for the experimental concentrations of 2-2 electrolytes are shown in Figure 1a. Magnesium chloride ($MgCl_2$) and calcium chloride ($CaCl_2$) are in the equilibrium as well as

Table 2. Experimental liquid phase compositions from synthetic pulps

Number Test	% mass fraction of equilibrium liquid phases with the respective solids	Density at 20°C (g.cm ⁻³)	Liquid phase composition (%w/w)				
			NaCl	KCl	MgCl ₂	CaCl ₂	H ₂ O
Test 1	98	1.200	16.62	1.29	2.50	3.89	75.70
Test 2	77	1.215	14.50	2.60	4.19	12.46	66.26
Test 3	71	1.230	9.90	3.10	4.60	12.84	69.55
Test 4	11	1.300	1.48	2.00	4.88	14.03	77.61
Test 5	98	1.370	0.32	0.02	5.55	28.19	65.92

Table 3. Experimental solid phase compositions from synthetic pulps

Number Test	% mass fraction of equilibrium solid phase with the respective liquids	Solid phases compositions (%w/w)				Solid phase identified by x-Ray diffraction
		NaCl	KCl	MgCl ₂	CaCl ₂	
Test 1	2	100	0	0	0	NaCl
Test 2	23	100	0	0	0	NaCl
Test 3	29	98	2	0	0	NaCl, KCl
Test 4	89	1	51	48	0	NaCl, KCl, Carnallite (KCl. MgCl ₂ .6H ₂ O) and Bischofite (MgCl ₂ .6H ₂ O)
Test 5	2	1	6	9	84	NaCl, MgCl ₂ .6H ₂ O, Tachyhydrite (CaCl ₂ .MgCl ₂ .12H ₂ O) and Antractite CaCl ₂ .6H ₂ O

Table 4. Liquid phase compositions calculated by the Pitzer's and Harvie's models

Number Test	Density at 20°C (g.cm ⁻³)	Liquid phase composition (%w/w)					Activity of water (a_w)
		NaCl	KCl	MgCl ₂	CaCl ₂	H ₂ O	
Test 1	1.200	15.25	1.53	2.50	5.20	75.52	0.729
Test 2	1.215	7.44	3.01	4.93	10.24	74.38	0.676
Test 3	1.230	5.01	2.59	6.10	12.67	73.62	0.642
Test 4	1.300	1.13	1.09	5.97	23.50	68.30	0.492
Test 5	1.370	0.15	0.26	18.68	15.40	65.52	0.298

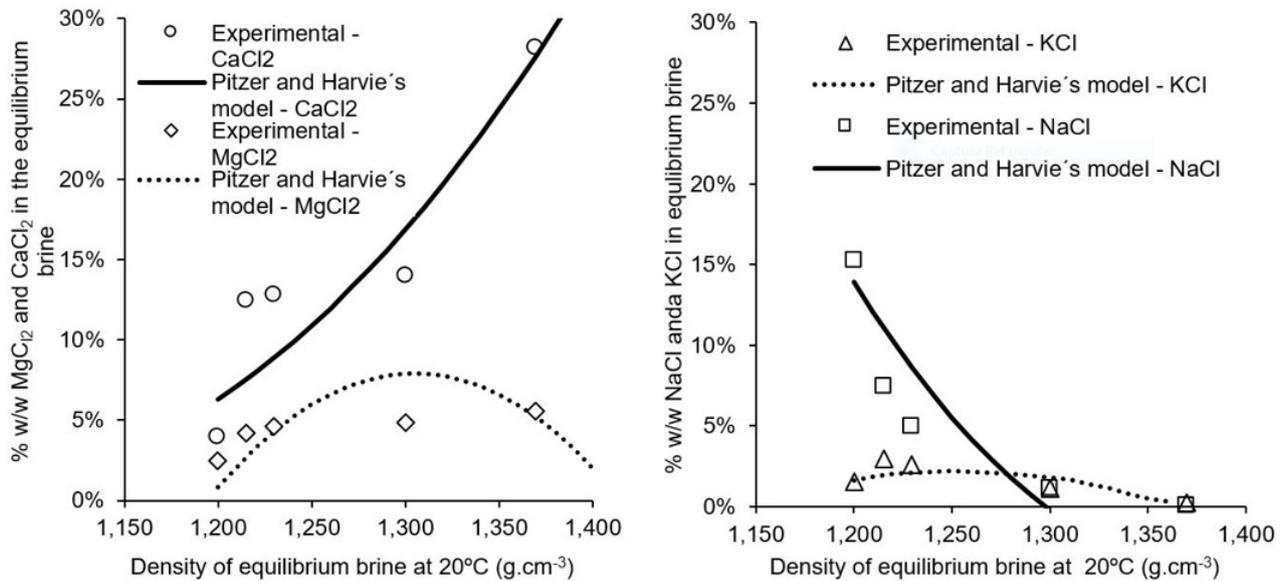


Figure 1. Comparison between predicted Pitzer and Harvie's model [7, 9] and experimental data for aqueous system Na-K-Mg-Ca-Cl at 20°C: (a) CaCl₂ and MgCl₂ and (b) KCl and NaCl.

the other salts found by the Pitzer's and Harvie's models. Figure 1b shows a good agreement between the experimental and calculated results for 1-1 electrolytes, sodium chloride (NaCl) and potassium chloride (KCl). The systems showed an interesting behavior, always crystallizing sodium chloride and reaching the saturation in KCl, with a density of about 1.230 g.cm⁻³ (test 3) at 20°C, where about of 2% w/w of solid phase composition was KCl.

Figure 2 shows that sodium chloride (NaCl) or Halite represented in diffractograms by the letter H precipitates in all tests, while potassium chloride (KCl) or Sylvite, indicated by the letter S may started to crystallize in test 3, but it was only identified in test 4 (Figure 2d). The carnallite (KCl.MgCl₂.6H₂O) and bischofite (MgCl₂.6H₂O) salts may have crystallized in test 4 (Figure 2d), but were not identified by X-ray. Tacahydrate (MgCl₂.CaCl₂.12H₂O) and anthracite (CaCl₂.6H₂O) could have precipitated in test 5 (Figure 2e), but were not identified by X-ray too.

3.2 Use of Pitzer and Harvie's Model to Evaluate the Separation of Saleable Salts from Brines Represented by the Na-K-Mg-Ca-Cl System

The Pitzer's and Harvie's models [7,9] were used to simulate the process to obtain saleable salts from natural brine containing Na-K-Mg-Ca-Cl. The composition of liquid phase obtained in the Test 1 was assumed as the same of feed brine due to its saturated condition in NaCl, commonly seen in most brines used to produce KCl.

A solar evaporation process has been designed for the extraction of potassium chloride from brines. The basic streams for the material balance around a single solar pond is shown in Figure 3 where: (i) leakage is the brine lost from

the pond through porous dikes and floors. The quantity of leakage is usually described in kg per day and it is a function of the pond area [13].

According proposed by Butts [14], it was assumed a leakage of 0.01 l kg/day/m²; (ii) the water evaporated is usually expressed in mm/day or kg/day/m². For steps 1, 2, 3 and 4, it was assumed 3.5, 2.8, 2.0 and 1.50 kg of water evaporated per day per m²; (iii) entrainment is related to the brine that is lost attached to the salts deposit. As the salt crystals grow or accumulate on the pond floor, voids are created and some brine is trapped therein. The quantity of entrainment is a function of the quantity and type of salt deposited. The entrainment is generally expressed as a weight percent of the combined salts in the deposit and the entrained brine. It was assumed an entrainment loss of 15% in all steps. Salts combined to entrainment are here denominated impregnated salts.

Generally, the brine concentrations throughout each solar pond are uniform and equal to the concentration in the brine that leaves each step. This observation is a key assumption for the pond material balance. It was assumed that the leakages and the exit brines have the same concentration, so these streams can be created as a single stream to simplify the material balance.

For fixed concentrations at the entrance and exit points of the pond, the material balance is represented by a system of five variables: flowrate of feeding brine, flowrate of exit brine, evaporation rate, amount and composition of salts formed and pond area. The brines and salts compositions were calculated by the Pitzer and Harvie's model [7,9], and it is described in item 3.1. Of these five variables, only two are independent. By establishing the value of any two of these variables, the system may be solved and the material balance is obtained.

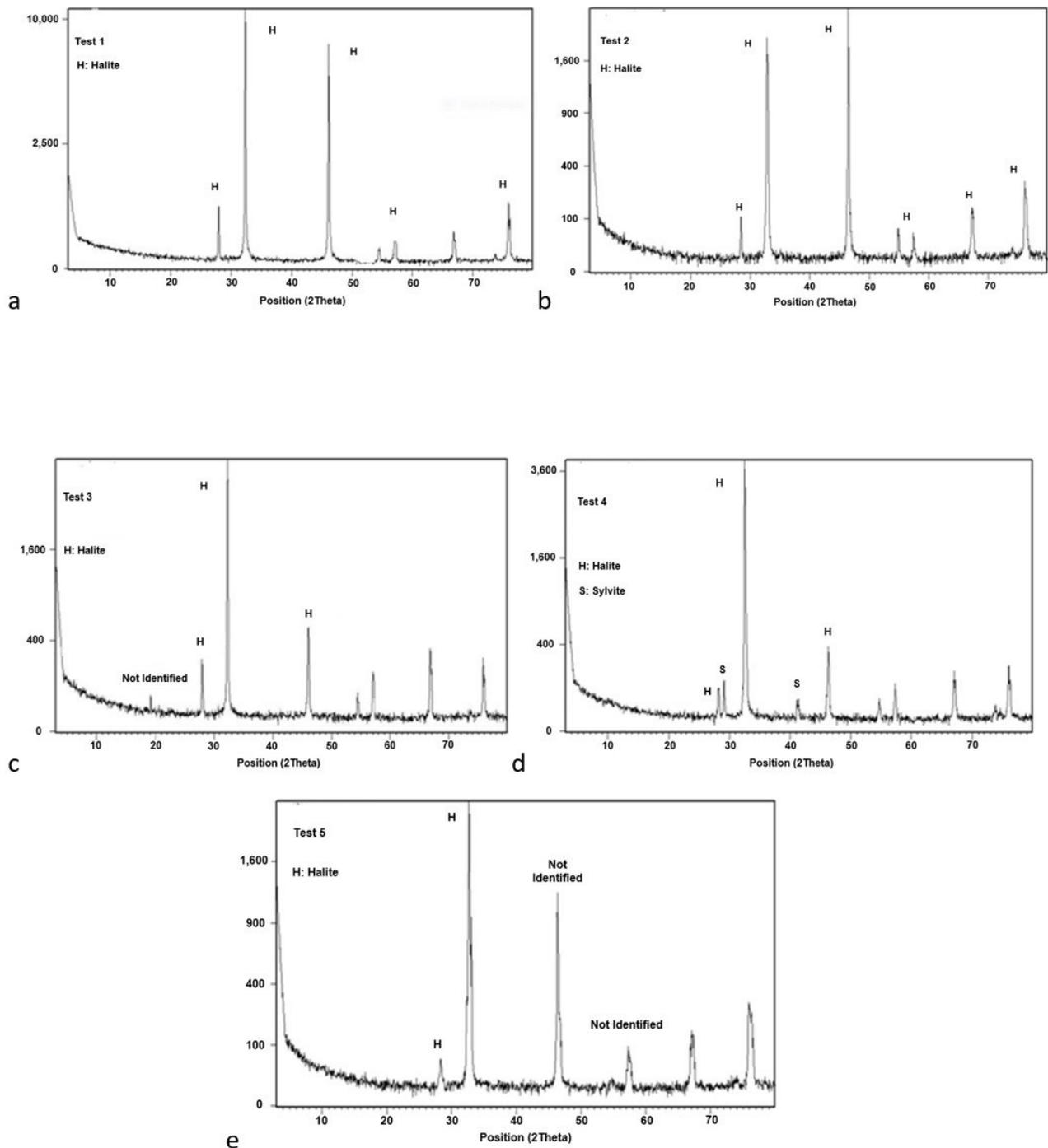


Figure 2. X ray diffractograms for crystallized salts produced in (a) Test 1, (b) Test 2, (c) Test 3, (d) Test 4 and (e) Test 5.

The overflow brine from Step 1 feeds the Step 2, the overflow brine from Step 2 feeds the Step 3 and the overflow brine from Step 3 feeds the Step 4. The overflow brine from Step 4 is called bittern brine, rich in the most soluble salts, like, $MgCl_2$ and $CaCl_2$. Table 5 shows the results of the material balance for Step 1, Step 2 and Step 3 using solar evaporation process to crystallize the desired salt. Table 6 shows the composition of feed and overflow brines.

According to the solubility calculated by the Pitzer and Harvie's model [7,9] and the material balance, a sequence of four stages could lead to the crystallization of following salts:

- ✓ Step 1: halite (84% w/w of NaCl);
- ✓ Step 2: sylvinite (58% w/w of NaCl + 16% w/w of KCl);

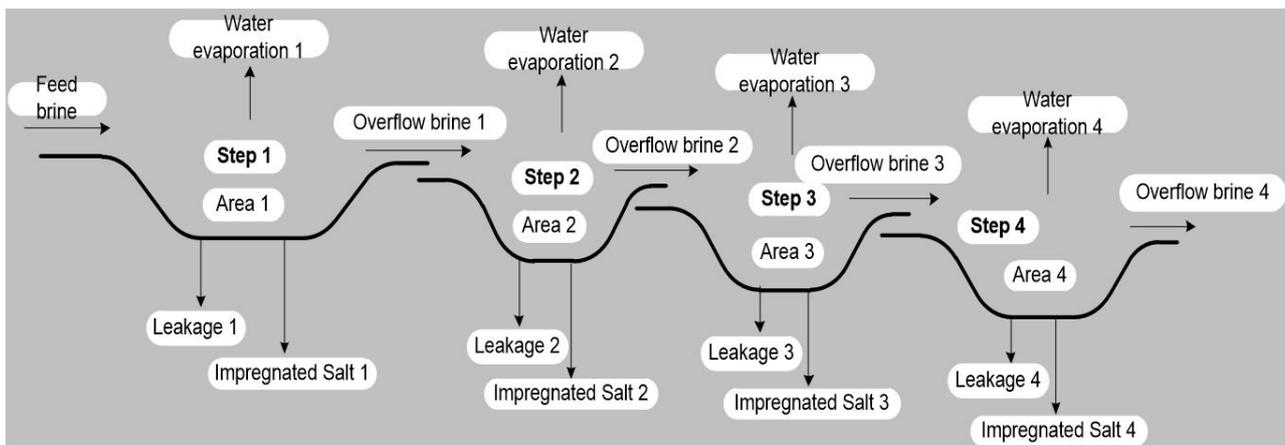


Figure 3. Basic streams of a solar pond for Step 1, 2, 3 and 4.

Table 5. Material mass balance results in solar ponds

	Step 1	Step 2	Step 3	Step 4
Pond area (m ²)	2,442	579	693	2,157
Feed brine (kg/h)	1000	482	385	300
Water evaporation (kg/h)	356	68	58	135
Leakage (kg/h)	1.12	0.27	0.32	0.99
Impregnated salts (kg/h)	160.43	29.29	27.17	93.88
Entrainment (kg/h)	24.06	4.39	4.08	14.08
Non impregnated salts (kg/h)	136.36	24.90	23.09	79.80
Overflow brine (kg/h)	482.40	385.25	300.00	71.00
% accumulated evaporated water	47	56	64	82
Composition of impregnated salts (%w/w)				
NaCl	72.66	56.47	6.41	3.49
KCl	0.45	15.46	4.11	3.29
MgCl ₂	0.74	0.92	61.01	4.90
CaCl ₂	1.56	1.82	3.66	63.41
Total water	24.59	25.33	24.81	24.91
Composition of non-impregnated salts (%w/w)				
NaCl	84	58	4	3
KCl	0	16	3	2
KCl.MgCl ₂ .6H ₂ O	0	0	4	6
MgCl ₂ .6H ₂ O	0	0	81	0
CaCl ₂ .6H ₂ O	0	2	0	75
Free water (% w/w)	16	24	9	14
% w/w of feed KCl crystallized (accumulated)	5	34	42	62
% w/w of feed KCl crystallized (in the respective Step)	5	30	7	20

- ✓ Step 3: A mixture of sylvinite (4% w/w of NaCl + 2% w/w of KCl), carnallite (4% w/w of KCl.MgCl₂.6H₂O) and bischofite (81% w/w of MgCl₂.6H₂O);
- ✓ Step 4: A mixture of sylvinite (3% w/w of NaCl + 2% w/w of KCl), carnallite (6% w/w of KCl.MgCl₂.6H₂O) and calcium chloride (75% w/w CaCl₂.6H₂O).

The feed brine in Step 1 is saturated in NaCl, but it is not saturated in other salts (KCl, MgCl₂ and CaCl₂), so this is the first salt to be crystallized in Step 1. Considering the amount of evaporated water (356 kg/h) and an evaporation rate of 3.5 mm/day, it will be necessary a pond area of about 2,442 m². Halite crystallized in Step 1 could be harvested and fed to a NaCl Industrial Plant. The brine density at 20°C changes from 1.200 to 1.215 g.cm⁻³, crystallizing approximately 451 kg of halite per 1,000 kg of evaporated water. Around 5% of entering potassium chloride is lost by impregnated brine in the salts.

Saturation in KCl is achieved in the overflow brine from Step 1 that feeds Step 2 (36.60 g/L of KCl). In the solar ponds of Step 2, KCl-rich salts (sylvinite) crystallize. The sylvinite crystallized in Step 2 is collected and fed to an industrial KCl Plant. The brine density at 20°C changes from 1.215 to 1.230 g.cm⁻³, resulting in the crystallization of approximately 433 kg of salts per 1,000 kg of evaporated water. About 30% of entering potassium will crystallize in this Step. Considering the amount of evaporated water in Step 2 (68 kg/h) and an evaporation rate of 2.8 mm/day, a pond area of about 579 m² will be necessary.

A mixture of sylvinite, carnallite and bischofite crystallizes in Step 3. This mixture could be harvested and fed to an industrial MgCl₂ Plant as well. The brine density at 20°C changes from 1.230 to 1.300 g.cm⁻³, crystallizing approximately 470 kg of salts per 1,000 kg of evaporated water. About 7% of entering potassium will crystallize in this Step. Considering the amount of evaporated water in Step 3 (58 kg/h) and an evaporation rate of 2.0 mm/day, a pond area of about 693 m² will be necessary.

A mixture of sylvinite, carnallite and calcium chloride crystallizes in Step 4. This mixture could be harvested and fed to an industrial CaCl₂ Plant as well. The brine density at 20°C changes from 1.300 to 1.370 g.cm⁻³, crystallizing approximately 696 kg of salts per 1,000 kg of evaporated water. About 20% of entering potassium will crystallize in this step. Considering the amount of evaporated water in

Table 6. Composition of initial and overflow brines, densities, KCl and MgCl₂ concentrations and total soluble solids

Component	Feed	Overflow Step 1	Overflow Step 2	Overflow Step 3	Overflow Step 4
NaCl (%w/w)	15.25	7.44	5.01	1.13	0.15
% w/w					
KCl	1.53	3.01	2.59	1.09	0.26
MgCl ₂	2.50	4.93	6.10	5.97	18.68
CaCl ₂	5.20	10.24	12.67	23.50	15.40
Total water	75.52	74.38	73.62	68.30	65.52
Density at 20°C (g.cm ⁻³)	1.200	1.215	1.230	1.300	1.370
KCl (g.L ⁻¹)	18.34	36.60	31.91	14.20	3.50
MgCl ₂ + CaCl ₂ (g.L ⁻¹)	92	184	231	383	467
Total soluble solids (g.L ⁻¹)	294	311	324	412	472

Step 4 (135 kg/h) and an evaporation rate of 1.5 mm/day, a pond area of about 2,157 m² will be necessary. The brine leaving Step 4 has small amounts of NaCl and KCl, therefore upon further processing (above a brine density of 1.370 g.cm⁻³) mainly magnesium and calcium salts are expected to crystallize.

Due to the low KCl and high MgCl₂ and CaCl₂ contents in the impregnated salts of Step 3 and 4, it is not recommended to feed them to an industrial KCl Plant, while it is suggested to feed the impregnated salt from Step 2, which contains a high KCl content (15.46% w/w) and low MgCl₂ (0.92% w/w) and CaCl₂ (1.82% w/w) contents. Considering feeding only the salt from Step 2, a total KCl recovery from the solar pond of 30% (only from Step 1), a KCl recovery in the industrial Plant of 70% and an on-stream factor of 90% (values assumed), the industrial Plant will result in about 48 ton of solid residues, 93 m³ of bittern brine, 127 ton of evaporated water and an area of 103 m² of solar pond per ton of KCl (60% w/w of K₂O) produced.

3 CONCLUSIONS

The experimental solubility data for Na-K-Mg-Ca-Cl aqueous systems compared well with the Pitzer's and Harvie's models. The models predicted the crystallization path found experimentally and was used to design a fractional crystallization process with four evaporation steps. This result will be useful for solubility prediction in more complicated systems and supply a theoretical basis for the extraction of salts from aqueous solution representing the Na-K-Mg-Ca-Cl aqueous systems, for instance, NaCl, KCl, KCl.MgCl₂.6H₂O, MgCl₂.6H₂O, MgCl₂.CaCl₂.12H₂O and CaCl₂.6H₂O.

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